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XPS studies of PMIDA adsorbed on Fe_3O_4 magnetic nanoparticles surfaces

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Magnetic nanoparticles (MNPs) based on Fe_3O_4 are currently the most widely used for biomedicine purposes such as magnetic resonance imaging, hyperthermia, drug delivery and others. Chemical modification of Fe_3O_4 MNPs surface via small organic molecules provides a simple means for their further functionalization with biomolecules. N-Phosphonomethyl iminodiacetic acid (PMIDA) is one of the promising reagents for surface modifications of various oxides including Fe_3O_4 [1]. Recently we assumed that PMIDA molecules are coordinating on the surface due to tridentate binding that involves P-O-Fe bonds [2].

The purpose of this work is comprehensive study of the mechanism of PMIDA binding with Fe_3O_4 nanoparticle surface by X-ray photoelectron spectroscopy (XPS) (K-Alpha+TM XPS system (Thermo Fisher Scientific, USA)).

We investigated the spectrum of initial Fe_3O_4 MNPs, PMIDA and PMIDA-modified nanoparticles (Fig. 1).

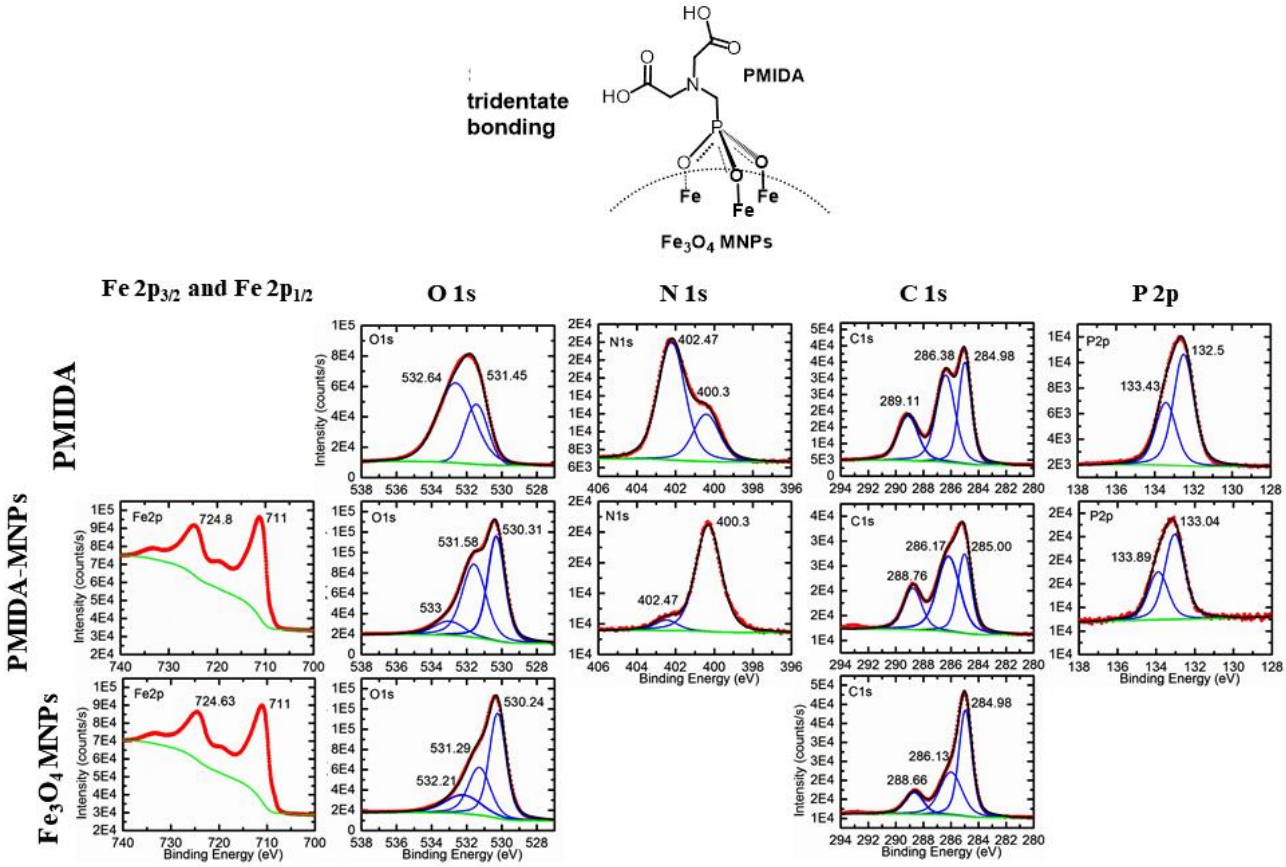

Figure 1. XPS spectra for Fe $2p_{3/2}$ and Fe $2p_{1/2}$, O 1s, N 1s, C 1s and P 2p binding energies of Fe_3O_4 MNPs, PMIDA and PMIDA-modified nanoparticles.

XPS spectrum of bare and modified MNPs shows the Fe2p doublet with same binding energy values), typical for magnetite. In O 1s binding region we observed a little shift of the band at 531.58 eV (compare with 531.45 eV and 531.29 eV corresponding to P-O of PMIDA and Fe_3O_4 MNPs) attributed to P-O-Fe and P=O···Fe bonds. Indirect confirmation of P-O-Fe bonds formation is the redistribution of the intensity of N 1s peaks with binding energy of 402.47 eV (minor) and 400.30 eV (major) for PMIDA-modified MNPs in comparison with spectrum of

PMIDA. In C 1s binding region of PMIDA-MNPs spectrum, the peaks centered at 285.00 eV, 286.17 eV, 288.76 eV can be attributed to C-C; C-N, C–P, C–O; and C=O electrons of phosphonic acids derivative and C-contain contaminants (e.g., CO_2) on the MNP surface, respectively. The P2p spectrum exhibited two peaks at 133.04 eV and 133.89 eV attributed to P $2p_{3/2}$ and P $2p_{1/2}$ and having a shift of about 0.5 eV to high energy in comparison with peaks for PMIDA. Thus, it can be displayed that all P atoms of phosphonic acid participate in to coordinating with Fe atoms on MNP surface.

Thus, the hypothesis about anchoring of PMIDA molecules to magnetic nanoparticle surface through a tridendate bonding involving P-O-Fe bonds was experimentally confirmed. We believe that obtained results will help to provide a better understanding of binding schemes for this phosphonate derivative with MNPs surface.

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1. A.M. Demin, A.G. Pershina, A.S. Minin, A.V. Mekhaev, V.V. Ivanov, S.P. Lezhava, A.A. Zakharova, I.V. Byzov, M.A. Uimin, V.P. Krasnov, L. Ogorodova, *Langmuir* **34**, 3449 (2018).
2. A.M. Demin, A.V. Mekhaev, A.A. Esin, D.K. Kuznetsov, P.S. Zelenovskiy, V.Ya. Shur, V.P. Krasnov, *App. Surf. Sci.* **440**, 1196 (2018).